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Optical and EXAFS studies of $NaNbO_3$ - $Gd_{1/3}NbO_3$ solid solutions

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$NaNbO_3$ based solid solutions are prospective environmentally-friendly materials for piezoelectric, pyroelectric, electrostrictive and energy storage applications. In the present work ceramics and flux-grown crystals of $(1-x)NaNbO_3$-$xGd_{1/3}NbO_3$ (NNG-x) solid solutions are studied in order to take a further insight into the nature of phase transition diffusion in $NaNbO_3$-based solid solutions. At high enough x values NNG-x compositions are known to exhibit a diffuse dielectric permittivity ε maxima [1].

Temperature-dependent optical studies of NNG crystals were carried out by the rotating polarizer method, using the Metripol (www.metripol.com) microscope system [2] and a precise heating stage (Linkam HFS91). False-color images showing values of $|\sin\delta| = |\Delta n\, L\, 2\pi/\lambda|$ (Δn – birefringence, L – crystal thickness, $\lambda = 600$ nm – light wavelength) and the orientation of the optical indicatrix at every point of the crystals were obtained in the temperature range 20 to 600 °C. Birefringence values were extracted from the $|\sin\delta|$ data.

Optical studies have shown that the value of $|\sin\delta|$ of pure $NaNbO_3$ exhibits an abrupt jump at 370 °C, corresponding to the well known first-order antiferroelectric phase transition. No such jumps are observed at higher temperatures. High-temperature phase transitions which occur at 480, 520, 575 °C according to the X-ray diffraction studies manifest themselves only through a change in the period of $|\sin\delta|$. Two types of optical extinction – symmetrical and parallel have been observed in two domains of the crystal below the phase transition and only parallel extinction at higher temperatures. This is in a total agreement with the earlier optical studies of $NaNbO_3$ crystals.

NNG-x crystals also display distinctive changes of birefringence which can be attributed to phase transition, though their dielectric permittivity maxima are diffused substantially. Up to the $\varepsilon(T)$ maximum the crystals remained uniform. However in the vicinity of the phase transition spontaneous splitting into small regions less than 0.001 mm in size with diffuse boundaries occurs and the distribution of the birefringence image becomes very messy. The origin for this non-uniformity may be a complicated domain structure arising as a result of the phase transition or coexistence of two phases over a wide temperature range. As the temperature increases the crystal gradually becomes more uniform as seen by the fact that the scale of the non-uniformity increases up to 0.05 mm well above the phase transition point.

Nb K-edge extended X-ray absorption fine structure (EXAFS) spectra of the pure NN and NNG-0.2 ceramics were measured in the transmission mode at the Synchrotron Radiation Source (SRS, Daresbury). Comparison of Fourier Transforms (FT) of Nb K-EXAFS spectra of NN and NNG-20 show that up to 4 Å they are very similar with peak amplitudes just slightly lower for the doped sample, implying that Gd impurities make a subtle effect on the Nb nearest environment. However FT EXAFS of the NN has more distinct peaks comparative to those for NNG-0.2 sample at distances higher than 4 Å from Nb, indicating a breakdown of ordering on the middle-range scale due to Gd impurity.

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